ABSTRACT

This thesis presents results on the role of methylaluminoxane (MAO) in the coordination polymerization of ethylene initiated by zirconocene and free radical polymerization of methyl methacrylate initiated by light. The effect of preparative conditions on the properties of the MAO such as methyl/aluminum molar ratio, mol% TMA and average molecular weight are explored. The effect of these properties on the rate of ethylene polymerization and catalytic activity in combination with Cp_2ZrCl_2 at 70°C and one atmosphere ethylene pressure in toluene are reported. The results show that high molecular weight MAO ($\bar{M}n$ >805) with a methyl/aluminum molar ratio of 1.65 and 32.5 mol% TMA content is necessary to produce a high molecular weight poly(ethylene) with high catalyst activities and high initial rates of polymerization.

Monomeric sterically hindered aryloxy derivative of TMA, ($AlMe(BHT)_2$), was synthesized and found to be inactive for the polymerization of ethylene in combination with Cp_2ZrCl_2. However, upon addition of TMA to the Cp_2ZrCl_2-$AlMe(BHT)_2$ catalyst system, a kinetic profile similar to that of Cp_2ZrCl_2-MAO system is observed with low rates of polymerization and catalytic activity. Ethylene polymerizations were carried out for the Cp_2ZrCl_2-MAO and Cp_2ZrCl_2-TIBDAO catalyst systems at one atmosphere ethylene pressure under different conditions like concentration of Cp_2ZrCl_2, concentration of MAO/TIBDAO and temperature. Effect of these parameters on Rp, catalyst activity and molecular weight are reported. The beneficial effect of added trimethylaluminum (TMA) on changing the kinetic profile from a decay to a steady state type was demonstrated.

MAO has been found to initiate the photopolymerization of MMA with unusual features. A linear increase in number average molecular weight and conversion with time has been observed. This behavior is reminiscent of the "living" radical polymerization of MMA with thermal and photoiniferters and indicative of an environment where the free radical has unusual stability. Kinetic features of MAO initiated photopolymerization of MMA show significant difference from that of photopolymerization initiated by TMA. The actual initiating species in case of MAO induced photopolymerization is found to be the residual TMA present in MAO.

Experimental evidences has been provided to conclude that the mechanism of photopolymerization of MMA is a free radical process. Presumably Wittig "ate" type of complex acts as the initiating species. All evidences thus point out to the unusual stability of the growing free radical in presence of MAO. It is proposed that the growing radical is trapped within the cages of the MAO oligomer clusters. These cages, consisting of Al-O-Al linkages, are similar to other three dimensional structures such as, zeolites and γ-Al_2O_3.